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Physical properties in the cluster-based magnetic-diluted triangular lattice antiferromagnets $Li_2Sc_{1-x}Sn_xMo_3O_8$

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Abstract. We have investigated the physical properties of the magnetic diluted triangular lattice antiferromagnetic system $Li_2Sc_{1-x}Sn_xMo_3O_8$. For all compounds, no mangetic ordering has been observed. On the other hand, the partial spin disappearing behavior is found in all Sn-substituted compounds except $x = 0$, which has been also observed in the similar magnetic system $LiZn_2Mo_3O_8$. Considering the relationship between the crystal structure and the magnetism, the partial spin disappearance is properly explained by a formation of the valence bond glass derived from the randomness effect

1. Introduction

Geometrical frustrated magnetism have attracted much attention because of their possibility to host novel phenomena. In particular, quantum spin frustrated magnets are expected to exhibit exotic ground states like a quantum spin liquid (QSL) state [1, 2, 3]. A strong spin frustration is realized in a characteristic lattice such as triangular, kagome (in 2D), face-centered cubic and pyrochlore lattice (in 3D). In realistic compounds, the highly frustrated spin liquid state is hard to be realized owing to the higher order magnetic interactions or coupling to other degrees of freedom such as lattice, valence, and orbital instabilities. Newly produced ground states may contain novel physics depending on characteristics of each compound.

Recently, we discovered $S = 1/2$ triangular lattice cluster antiferromagnet $Li_2ScMo_3O_8$ [4]. In this compound, Mo_3 trimers form a triangular lattice, and the Mo_3 layers and nonmagnetic cations are stacked alternately as shown in the Fig.1 (a) and (b). The magnetic state of $[Mo_3]^{11+}$ in $Li_2ScMo_3O_8$ is $S = 1/2$ as shown in Fig. 1(c). Then, $Li_2ScMo_3O_8$ is categorized as the $S = 1/2$ triangular lattice antiferromagnets. In our previous investigations, it has been found that $Li_2ScMo_3O_8$ is a powerful candidate of the QSL. In the similar magnetic systems, the isostructural $Li_2InMo_3O_8$ exhibits a conventional magnetic ordering with 120° spin configuration [4], and the other magnetic system $LiZn_2Mo_3O_8$ shows a formation of the valence bond solid on the honeycomb sublattice without magnetic ordering [5]. Thus, the Mo_3 trimer-based triangular lattice antiferromagnets exhibit various phenomena based on a frustrate magnetism. Therefore,

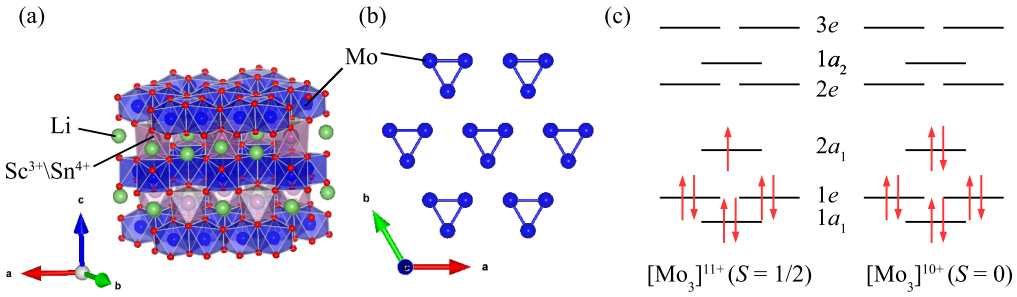

Figure 1. (Color online) (a) The crystal structure of $Li_2Sc_{1-x}Sn_xMo_3O_8$. (b) Mo_3 trimers forming a triangular lattice. (c) Schematic $4d$ orbital energy level of the $[Mo_3]^{11+}/[Mo_3]^{10+}$ trimer with the electron configurations in $Li_2Sc_{1-x}Sn_xMo_3O_8$.

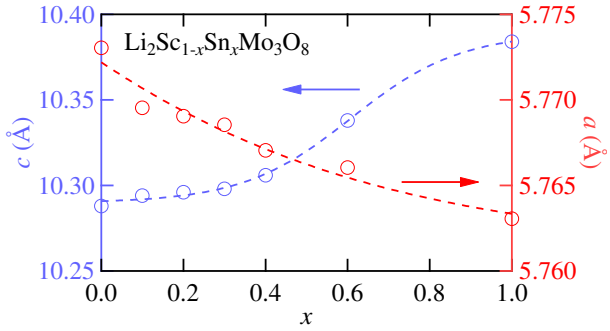

Figure 2. (Color online) The trigonal lattice parameters a and c in $Li_2Sc_{1-x}Sn_xMo_3O_8$ as a function of x. The dashed lines are a guide to the eye.

it is necessary to reveal the different ground state among Mo_3 cluster compounds, which will help understanding the QSL behavior in $Li_2ScMo_3O_8$.

In this work, we report on the physical properties of the magnetic diluted $Li_2Sc_{1-x}Sn_xMo_3O_8$ system. The Sn-substitution reduces the valence of Mo, which reflects the magnetic dilution to the $S = 1/2$ triangular lattice system by the nonmagnetic $[Mo_3]^{10+}$ trimers ($S = 0$) instead of the $[Mo_3]^{11+}$ trimers ($S = 1/2$). That is, the chemical formula can be written as $Li_2Sc_{1-x}Sn_x[Mo_3]^{11+}{}_{1-x}[Mo_3]^{10+}{}_xO_8$. For all Sn-substituted compounds without $x = 0$, the partial spin disappearing behavior is found similar to $LiZn_2Mo_3O_8$. The relationship between the magnetic properties and the crystallographic structure for both systems indicates that the randomness is the possible origin to emerge the partial spin disappearance caused by the valence bond glass formation.

2. Experimental Methods

Polycrystalline samples of $Li_2Sc_{1-x}Sn_xMo_3O_8$ were prepared using conventional solid-state reactions. These samples were characterized by powder x-ray diffraction (XRD) on a diffractometer with Cu$K\alpha$ radiation. As shown in Fig. 2, the lattice parameters a and c in $Li_2Sc_{1-x}Sn_xMo_3O_8$ monotonically vary with increasing x, suggesting the successful solid solution. The temperature dependence of the magnetization was measured under several magnetic fields up to 7 T by using a magnetic property measurement system (MPMS; Quantum

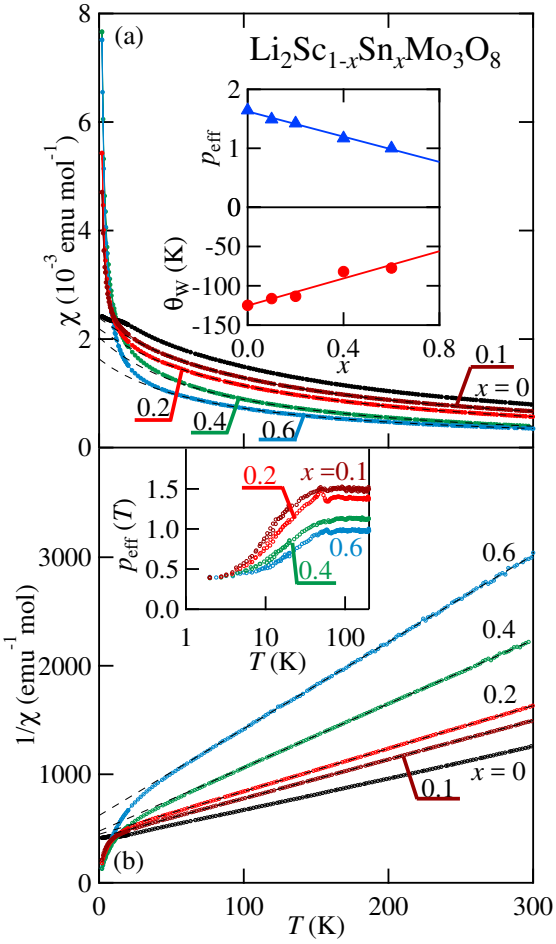

Figure 3. (Color online) (a) The temperature dependence of the magnetic susceptibility χ in $Li_2Sc_{1-x}Sn_xMo_3O_8$. The inset shows the composition dependence of the the effective paramagnetic Bohr magneton $p_{\rm eff}$ and the Curie-Weiss temperatures at the high-temperature region. (b) The $1/\chi$ vs. T plot. The inset shows the temperature dependence of the normalized effective paramagnetic Bohr magneton $p_{\rm eff}(T)$.

Design) equipped at the LTM Research Center, Kyoto University. Magnetization measurements up to 60 T were performed using an induction method with a multilayer pulse magnet at the Ultra-high Magnetic Field Laboratory of the Institute for Solid State Physics at the University of Tokyo.

3. Results and Discussion

Figure 3(a) shows the temperature dependence of the magnetic susceptibility χ in $Li_2Sc_{1-x}Sn_xMo_3O_8$. For all compositions, they obey in the Curie-Weiss law in the high temperature region and show no anomaly accompanied by a magnetic ordering or a spin glass freezing. The Weiss temperature θ_W and the effective paramagnetic Bohr magneton $p_{\rm eff}$ monotonically vary with increasing Sn substitution x, which is plotted in the inset of the Fig. 3(a). The reduction of $p_{\rm eff}$ by increasing x suggests the increase of the nonmagnetic $[Mo_3]^{10+}$ trimers instead of the $S = 1/2$ $[Mo_3]^{11+}$ trimers. The reduction of θ_W is originated in the

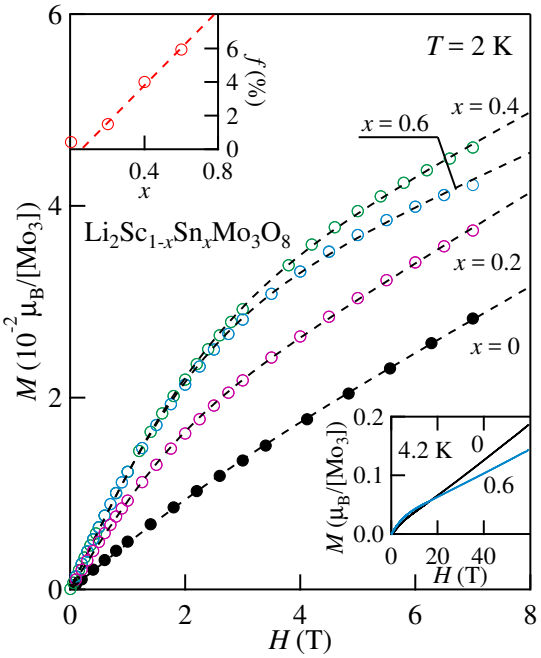

Figure 4. (Color online) The isothermal magnetization at 2 K (circles) and those fitting curves with Eq. (1). The upper inset shows the percentage of free spins. The downer inset shows the isothermal magnetization up to $H = 60$ T at 4.2 K only for $x = 0$ and 0.6.

reduction of the number of the magnetic couplings from the magnetic dilution.

For all composition except $x = 0$, χ shows an enhancement and a deviation from the Curie-Weiss law in the low temperature region. In addition, as shown in Fig. 3(b), a change in the slope of $1/\chi$ as a function of temperature is observed at low temperatures, suggesting the partial disappearance of the paramagnetic spins. The inset of Fig. 3(b) shows the temperature dependence of $p_{\rm eff}$, estimated using the relation,

$$p_{\rm eff} \simeq \sqrt{\frac{8}{d\chi^{-1}/dT}}. \tag{1}$$

For all Sn-substituted compounds, $p_{\rm eff}$ gradually reduces with decreasing temperature. This behavior is very similar to the similar magnetic compound $LiZn_2Mo_3O_8$, in which the partial disappearance of the paramagnetic spins has been explained by the construction of a valence bond solid on the honeycomb sublattice. The the partial spin-disappearance in the $Li_2Sc_{1-x}Sn_xMo_3O_8$ system is also explained by a formation of partial spin singlet. The finite $p_{\rm eff}$ value in low temperatures means the presence of the free spins which have been orphaned by the partial spin singlet formation.

Figure 4 shows the isothermal magnetization measured in the field up to $H = 7$ T at $T = 2$ K. For all Sn-substituted compounds, M-H curves show the nonlinear behavior. The deviation from the linear relationship $M \propto H$ becomes larger with increasing x, indicating that the contribution of free spins becomes large with increasing x. In order to estimate the amount of free spins, we analyze the magnetization within the framework of the model that M is contributed by two components from the singlet-formed spins and the nearly free spins,

$$M(H,T) = \chi(T)H + N_A\mu_B f S_f g_f B_s(g_f S_f H\mu_B/k_B(T-\theta_f)), \tag{2}$$

Table 1. Results of fits to the isothermal magnetization data using the formula described in text. The parameters g_f and S_f are fixed to 2 and 0.5, for respectively.

x	f(%)	θ_f(K)	g_f	S_f	χ (emu/mol-$[Mo_3]^{11+}$)
0	0.43(1)	0.020(2)	2	0.5	0.00191(3)
0.2	1.49(2)	0.65(2)	2	0.5	0.00258(3)
0.4	4.00(5)	0.26(2)	2	0.5	0.00301(7)
0.6	5.93(6)	0.38(3)	2	0.5	0.00381(9)

where χ represents the susceptibility derived from the singlet-formed spins, and S_f, g_f, and θ_f denote, the Lande g-factor, spin quantum number, and Weiss temperature for early free spins. The symbols H, N_A, k_B, μ_B and B_s represent the magnetic field, the Avogadro number, the Boltzman constant, the Bohr magneton, and the Brillouin function, respectively. The parameter f represents the percentage of free spins against the magnetic $[Mo_3]^{11+}$ trimers. The fitting results are listed in Table 1. The estimated values of θ_f are very small, indicating almost no correlation among the free spins. The upper inset shows the x dependence of the estimated f value. For all Sn-substituted compounds, the contribution of the free spin to the magnetization process is relatively larger than that of the non-substituted compound. Considering that the f value is relatively small in $x = 0$ and remarkably increases with increasing x, the main part of the free spin in the low temperature phase would be derived from the randomness effect. Note that the amount of free spins should be due to extrinsic factors, for example, defects and impurity spins because of the finite value of f in $x = 0$. The magnetization process up to 60 T only for $x = 0$ and 0.6 are shown in the downer inset of Fig. 4. Neither saturated behavior nor field-induced transition is observed and each M shows linear behavior against H in the high magnetic field region, indicating that the spin singlet is not broken up to 60 T.

For $Li_2Sc_{1-x}Sn_xMo_3O_8$ and $LiZn_2Mo_3O_8$, the similar $p_{\rm eff}$ reduction has been observed. However, such the reduction is observed only in the system with the crystallographic disorder. In the case of $LiZn_2Mo_3O_8$, previous studies have clarified the presence of the mixture of Li and Zn ions [6]. And in the case of $Li_2Sc_{1-x}Sn_xMo_3O_8$, the intensional randomness is present. Thus, it is reasonable to think that the partial spin singlet formation to make the reduction of $p_{\rm eff}$ is caused by the randomness. Such a behavior is also observed in the triangular lattice $Sc_2Ga_2CuO_7$ [8] and $Ba_3IrTi_2O_9$ [9], and the kagome lattice Herbertsmithite $ZnCu_3(OH)_6Cl$ [10] and $ZnCu_3(OH)_6SO_4$ [11]. They also have crystallographic disorders of magnetic/nonmagnetic ions on the frustrated lattice. In the theoretical prediction, the randomness-induced valence bond glass model can explain the partial disappearance of paramagnetic spins [7]. In this model, the appearance of a small fraction of free spins to produce the Curie susceptibility is also predicted; leave some unpaired free spins would be orphaned by the random dimer spin pairing. Therefore, the origin of the the valence bond glass behavior observed in the Mo_3 cluster systems would be the randomness effect derived from the magnetic dilution. And such randomness effect to emerge the valence bond glass behavior would be characteristic in the highly frustrated magnets.

4. Summary

We studied the physical properties of the magnetic diluted triangular lattice antiferromagnetic systems $Li_2Sc_{1-x}Sn_xMo_3O_8$. With increasing of Sn substitution x, the nonmagnetic $[Mo_3]^{10+}$ clusters increase instead of the $S = 1/2$ $[Mo_3]^{11+}$ clusters, which results in the introduction of a magnetic dilution to the magnetic systems on the triangular lattice. For Sn substituted compounds, the partial disappearance of paramagnetic spins without magnetic orderings has been observed. This behavior is also observed in the similar magnetic system $LiZn_2Mo_3O_8$. Considering the relationship between the magnetic properties and the crystallographic structure for both systems, the randomness effect is the possible driving-force to emerge the partial

disappearance of paramagnetic spins caused by the valence bond glass formation. Furthermore, it is concluded that the quantum spin liquid behavior observed in $Li_2ScMo_3O_8$ is an essential character on the triangular lattice antiferromagnets without a randomness effect.

Acknowledgments

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